

ULTRA-FAST LASER DESORPTION / LASER IONIZATION MASS SPECTROMETRY FOR THE ORGANIC ANALYSIS OF STARDUST SAMPLE RETURN

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Introduction: The STARDUST sample return capsule is anticipated to provide 500-1000 cometary particles $\geq 15 \mu\text{m}$ in size [1]. These were collected during the 340 km flyby of Comet P/Wild-2 and impacted the aerogel collection medium at a relative velocity of $\sim 6.1 \text{ km}\cdot\text{s}^{-1}$ [1]. Hypervelocity impact studies suggest that some fraction of the original organic inventory [2] of collected particles ought to remain intact, although there is likely to be a significant amount of devolatilization and disassociation of the lower mass organic fraction [3, 4].

Analysis of the organic composition of these particles will potentially provide valuable clues to the inventory and distribution of organic molecules in interplanetary and interstellar environments, as well as their evolution, survival, transport, and transformation from molecular clouds and the diffuse interstellar medium to their incorporation into solar system materials [5].

We have developed a new generation ultra-fast laser desorption / laser ionization mass spectrometry (*ultra-L²MS*) recently completed at Johnson Space Center (JSC) capable of perform *in situ* organic analysis of STARDUST (see Fig. 1).

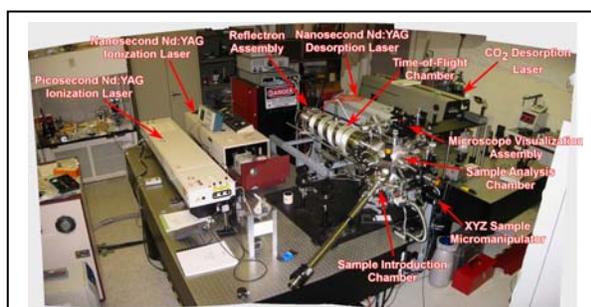


Figure 1: Layout of *ultra-L²MS* instrument. The main vacuum assembly including the time-of-flight reflectron and sample analysis chamber is situated between the two laser tables. The laser table on the left supports the picosecond Nd:YAG and nanosecond Nd:YAG laser systems that provide a versatile laser ionization source. The laser table on the right supports the line-tuned CO₂ laser and a nanosecond Nd:YAG laser that provides a versatile laser desorption source.

Instrumentation: The operation of the *ultra-L²MS* system is based on heritage from the Stanford $\mu\text{L}^2\text{MS}$ instrument [6]. In the $\mu\text{L}^2\text{MS}$ technique a rapid non-thermal heating event ($dT/dt \sim 10^8 \text{ K}\cdot\text{s}^{-1}$) initiated by a focused infrared (IR) laser pulse which is used to affect the desorption of constituent neutral molecules with little or no fragmentation from the sample, housed in a vacuum chamber. After an appropriate time delay aromatic species in the desorbed plume of material are selectively ionized with a nanosecond pulsed ultraviolet laser pulse using (1+1)-REMPI. Ionized aromatic species are then analyzed by mass in a reflectron time-of-flight mass spectrometer.

The *ultra-L²MS* instrument has a similar mode of operation but utilizes an ultrafast picosecond/femtosecond UV laser ionization source. Ultrashort pulsed lasers represent promising new ionization sources for the detection of molecules desorbed from surfaces. The enhanced absorption rates generated by highpower ultrashort pulses make it possible to “outrun” the neutral fragmentation channels, which are prevalent when employing nanosecond excitation of molecular species [7,8]. The ultra-fast picosecond/

femtosecond laser ionization scheme can therefore be regarded as an efficient, universal and soft ionization source for many types of molecular species [9-11]. Additionally the *ultra-L²MS* instrument has multiple lasers which can be configured to provide versatile laser desorption schemes with variable spatial resolution down to $1 \mu\text{m}$.

Preliminary Results & Discussion: To date every sample of STARDUST equivalent aerogel that has been investigated by *ultra-L²MS* has shown some level of organic contamination (see Fig. 2). This is probably inevitable due to the relatively high sticking coefficient of the SiO₂ surface, particularly in respect to polar organics, in combination with the extraordinary high surface area of the gel. Clearly any analysis of returned aerogel will need to be tempered with this knowledge.

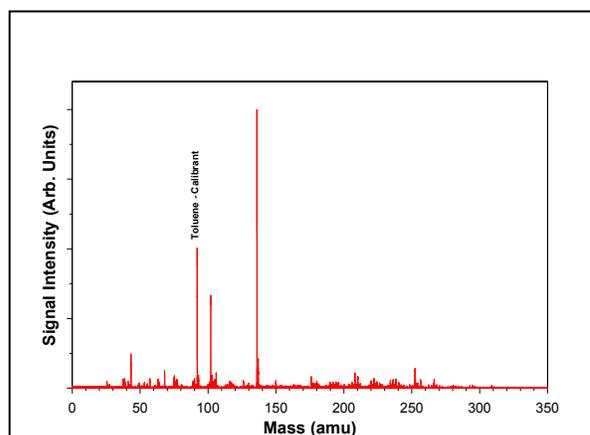


Figure 2: Aerogel background as determined by *ultra-L²MS*, mass peak at 92 amu is introduced for mass calibration.

Utilizing micron-sized fragments of carbonaceous chondrite matrix as simulated sample return particles it is routinely possible to obtain a complete mass spectra characterization of individual particles (see Fig. 3).

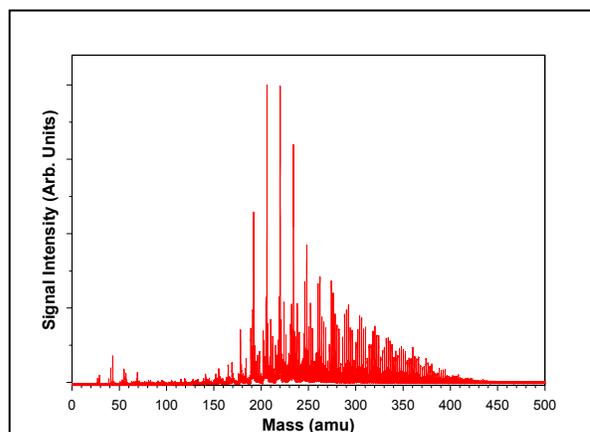


Figure 3: *ultra-L²MS* characterization of a single 10- μm sized particle of Allende (CV3) matrix.

Conclusions: *ultra-L²MS* offers a unique analytical approach to the organic analysis of aerogel captured cometary particles > 1 μm in size contain, with detection sensitivities at the part per million (ppm) level or above. The observed distribution of any observed organic species can be correlated with an already established reference database of organic species from carbonaceous chondrites and interplanetary dust particles [6]. Since the *ultra-L²MS* technique is a direct surface analysis that does not require sample pre-treatment and is mineralogically non-destructive it is suitable for consortium analysis. Hence correlations existing between any observed organic species and the mineralogical and/or isotopic characterization of the same particle by TEM and nanoSIMS are possible.

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References: [1] Zolensky *et al.*, LPSC 2004; [2] Cottin *et al.*, *Planet. & Space Sci.* **47**, 1141 (1999); [3] Bass *et al.*, *Bullet. AAS* **30**, 1 (1998); [4] Bass *et al.*, LPSC (1999); [5] Greenberg & Muñoz Caro, *Astrochemistry: From Molecular Clouds to Planetary Systems* (2000); [6] Clemett & Zare, *IAU Symp. 178: Molecules in Astrophysics: Probes & Processes* (1996); [7] Kilic *et al.*, *J. Phys. Chem. A* **101**, 817 (1997); [8] Szaflarski & El-Sayed, *J. Phys. Chem.* **92**, 2234 (1988); [9] Matsumoto *et al.*, *Anal. Chem.* **69**, 4524 (1997); [10] Grun *et al.*, *Int. J. Mass Spectrom.* **185**, 307 (1999); [11] Mollers *et al.*, *Org. Mass. Spectrom.* **27**, 1393 (1992)